

LOW-CARBON 3D-PRINTABLE MAGNESIUM OXYCHLORIDE COMPOSITES WITH INDUSTRIAL BY-PRODUCT FILLERS

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ABSTRACT. This research focuses on the development and characterization of 3D printed magnesium oxychloride cement (MOC)-based composite material. As an environmentally friendly alternative to conventional binders such as Portland cement, MOC offers significant sustainability benefits, including lower embodied energy and reduced CO₂ emissions. To further enhance its environmentally friendly character, ground granulated blast furnace slag (GVS), an industrial by-product, was incorporated as a supplementary filler instead of standard silica sand filler. This approach not only promotes the recycling of industrial byproducts but also reduces the consumption of natural resources. The prepared composite sample was successfully 3D printed and demonstrated the formation of the desired MOC phase 5, confirming its suitability for additive manufacturing. The sample was analyzed to determine its chemical and phase composition as well as macro- and microstructure. These findings highlight MOC phase 5 as a promising binder system for sustainable and efficient 3D printing applications.

KEYWORDS: Slag, magnesium oxychloride cement, 3D printing, sustainable composites.

1. INTRODUCTION

Amid growing efforts toward a more sustainable society, extensive research has been devoted to the development of environmentally friendly construction materials. In the cement industry, one such promising alternative to conventional Portland cement is magnesium oxychloride cement (MOC). The primary drivers behind the increasing research interest in MOC are its significantly lower CO₂ emissions associated with production compared to Portland cement, as well as its excellent mechanical properties. MOC is a nonhydraulic binder made from magnesium oxide, magnesium chloride, and water [1]. Based on the ratio of the raw materials, temperature, and other conditions, various phases are known in the MgO-MgCl₂-H₂O system. Among them are phases stable at temperature above 100 °C: phase 2 (2Mg(OH)₂·MgCl₂·4H₂O) and phase 9 (9Mg(OH)₂·MgCl₂·5H₂O) and phases stable at laboratory temperature: phase 3 (3Mg(OH)₂·MgCl₂·8H₂O) and phase 5 (5Mg(OH)₂·MgCl₂·8H₂O) [2, 3]. Out of those known phases, MOC phase 5 has the highest mechanical strength and has the potential to bond

various fillers, including waste materials, into its structure [4, 5]. It can also absorb CO₂ to form carbonates, which makes it more “carbon-neutral” than ordinary Portland cement [6].

Steel slags are by-products formed during the steel production process. Depending on the type of production equipment used, they are classified as furnace slags or ladle slags. Their chemical composition varies based on the specific production method, particularly whether the process is basic or acidic, as well as other operational conditions. The primary chemical constituents typically include CaO, Al₂O₃, SiO₂, and FeO_x. Ladle slags generally contain lower amounts of iron oxides, whereas furnace slags tend to have reduced levels of CaO and Al₂O₃. The exact composition is further influenced by the raw material charge and the course of the production process. Blast furnace slag is a waste material produced during the production of pig iron in the blast furnace. In 2023, crude steel production in the European Union and the United Kingdom reached approximately 140 million tonnes. This level of output resulted in around 20 million tonnes of blast furnace slag and 16 million tonnes

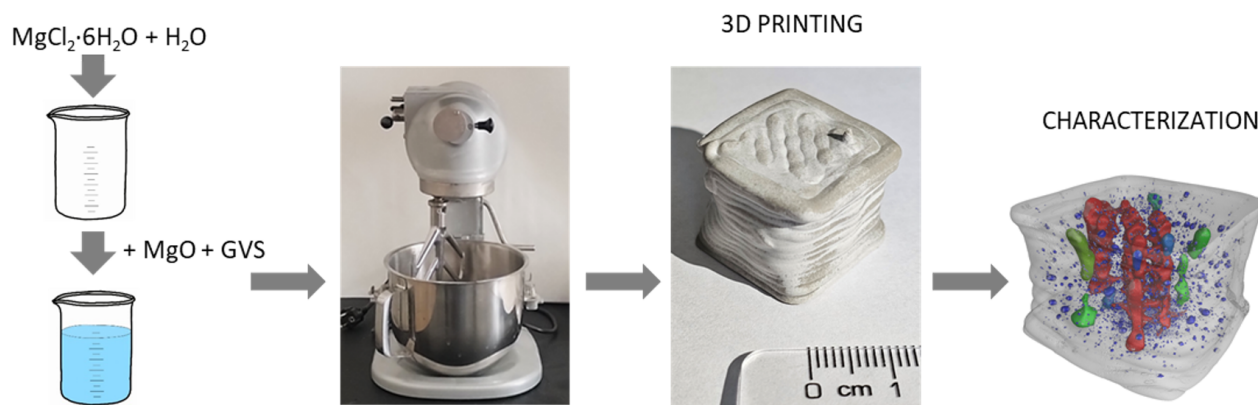


FIGURE 1. Scheme of the experimental work.

of steelmaking slag. More than 33 million tonnes – over 91 % of the total slag produced – were recycled. These by-products are primarily used in construction, agriculture (e.g., as fertilizers), and metallurgical processes. Rapid cooling of molten slag produces a glassy, noncrystalline material known as granulated blast furnace slag, which demonstrates strong cementitious properties in combination with Portland cement [7, 8].

Given MOC's ability to bond various fillers and waste materials into its structure, incorporating different types of industrial by-products and solid wastes into MOC has become a promising strategy for enhancing its properties while promoting sustainable waste management. For example, industrial waste materials: red mud, biomass fly ash, and copper slag, as supplementary cementitious materials, were used in MOC to improve its water resistance. Not only did those industrial waste materials improve water resistance, but they also improved the mechanical strength of the resulting material [9]. Lithium slag produced after extracting lithium from spodumene was used in MOC as well. Even though the slag prolonged the setting time of MOC and worsened its mechanical properties, it improved water resistance [10]. Other than that, waste wood, waste gypsum, and others were also used in MOC [11, 12].

This paper focuses on the characterization of an environmentally friendly composite material – MOC phase 5 – fabricated using 3D printing with the addition of ground granulated blast furnace slag (GVS). The 3D printed composite was then characterized by various analytical methods (XRF, XRD, SEM, EDS) to determine its chemical, phase composition, and microstructure. The quality of the printed sample, including structural defects and internal porosity, was analysed using X-ray computed micro-tomography (XCT).

2. EXPERIMENTAL

At first, GVS was ground and sieved to produce a fraction in the size range 0–0.5 mm. GVS was then

studied using XRD to determine the phase composition. For the preparation of MOC-based material, the following chemical substances were used: MgO of p.a. purity (Penta, Czech Republic), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ of p.a. purity (Lachner, Czech Republic), and GVS (Třinecké železářny, a.s., Czech Republic), and milled by LB Cemix Ltd., Czech Republic, in Kotouč Štramberk plant. The composition of the prepared sample can be seen in Table 1. The amount of GVS in the prepared mixture was determined experimentally to achieve optimal rheological properties for the printing process. The overall process is schematically visualized in Figure 1.

The phase composition was analyzed by X-ray diffraction (XRD). Chemical composition was studied by X-ray fluorescence (XRF) and Energy-dispersive spectroscopy (EDS). Morphology of the fracture surface was studied using Scanning Electron Microscopy (SEM). The structure of the prepared sample was analyzed by optical microscopy (OM). To facilitate structural analysis, volumetric data were acquired via X-ray computed micro-tomography (XCT), enabling full-field 3D characterisation of the sample's porous architecture.

Sample	MgO	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	Water	GVS
MOC-GVS	88.73	89.52	55.52	246.7

TABLE 1. Compositions of prepared samples (g).

3. RESULTS AND DISCUSSION

GVS was studied in terms of chemical composition and phase composition using XRF and XRD, respectively. The chemical composition of the analysed GVS is dominated by CaO (57.4 wt.%) and SiO_2 (26.5 wt.%), with moderate amounts of MgO (5.8 wt.%) and Al_2O_3 (5.2 wt.%). Minor components include SO_3 (1.8 wt.%), K_2O (0.5 wt.%), Na_2O (0.2 wt.%), and trace amounts of Fe_2O_3 , TiO_2 , MnO, SrO, and Cl. Detailed composition is listed in Table 2. The CaO/ SiO_2 ratio is 2.17. This ratio is relatively high, indicating that the slag is highly basic and exhibits strong hydraulic reactivity,

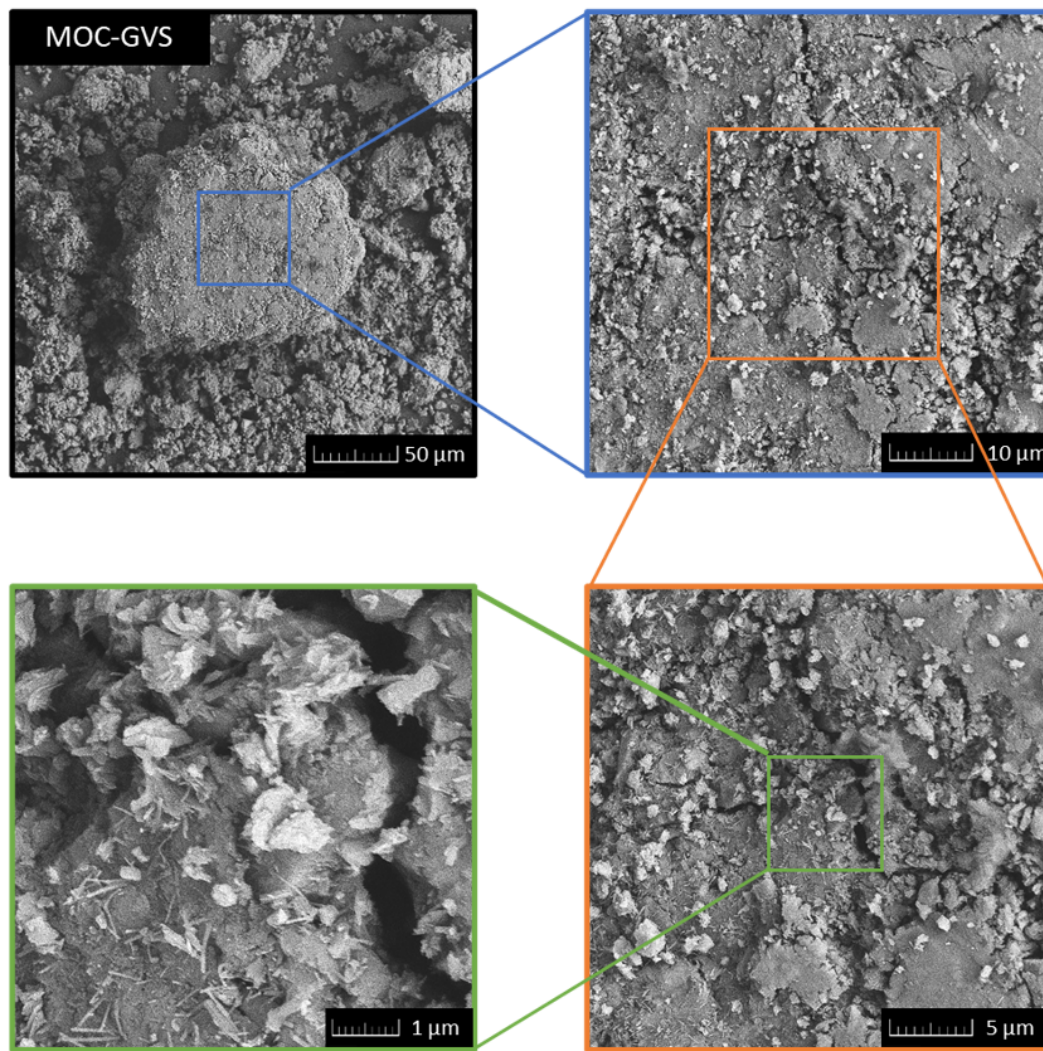


FIGURE 2. The SEM micrographs of MOC-GVS.

making it suitable for use as an active additive in cement or as a precursor for alkali-activated materials (geopolymers).

Component	wt.%
Na ₂ O	0.2
MgO	5.8
Al ₂ O ₃	5.2
SiO ₂	26.5
SO ₃	1.8
Cl	0.1
K ₂ O	0.5
TiO ₂	0.5
CaO	57.4
MnO	0.1
Fe ₂ O ₃	0.6
SrO	0.2

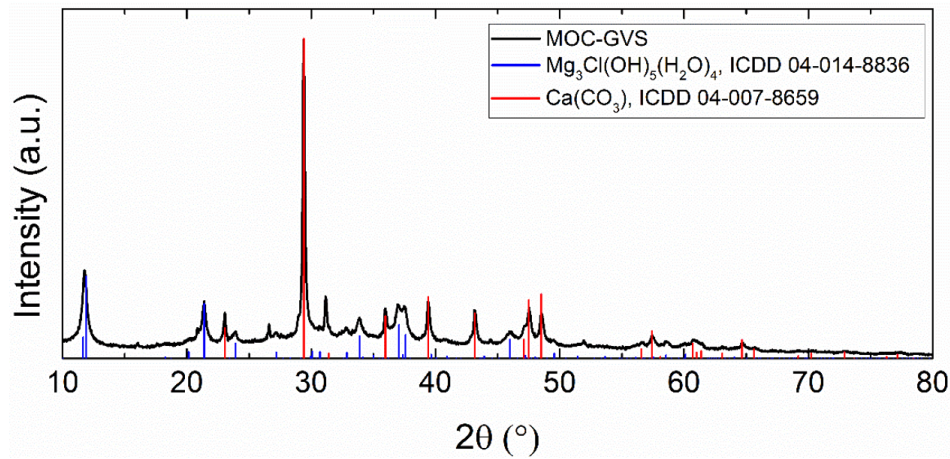
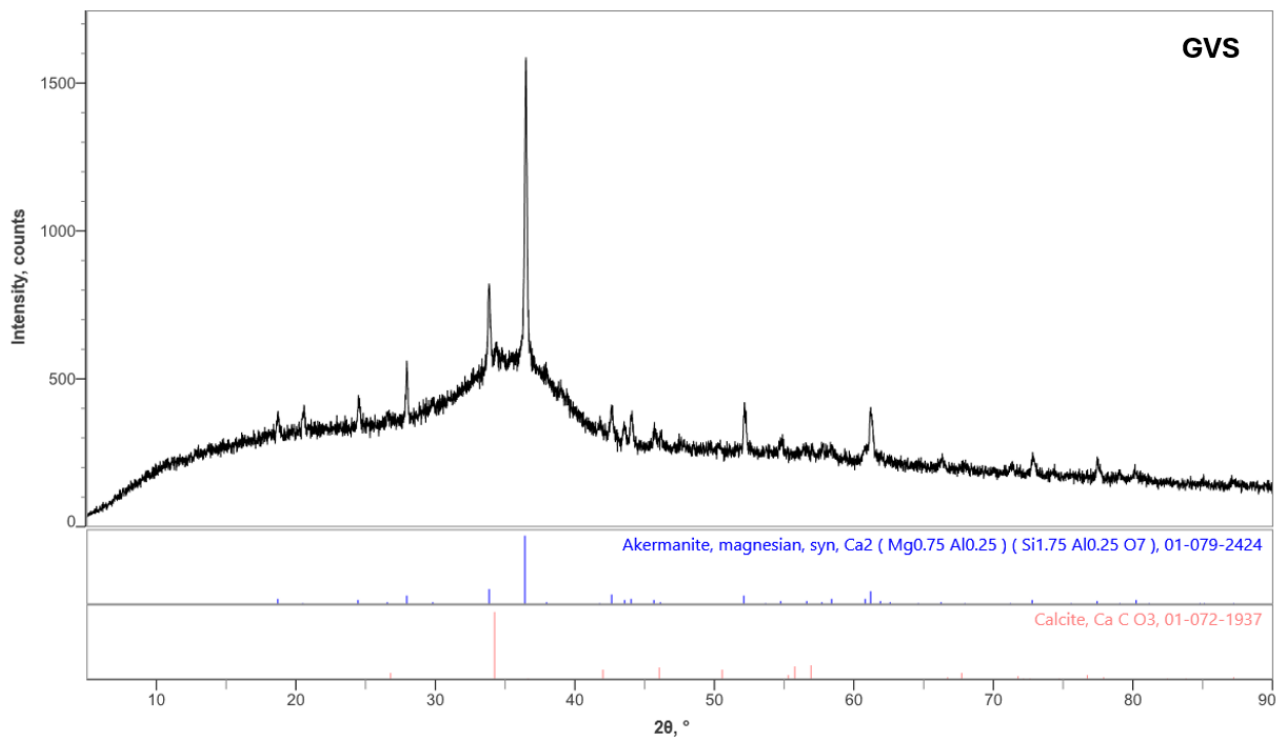
TABLE 2. Chemical composition of GVS obtained by XRF in wt.%.

The diffractogram shows a broad diffuse maximum between 20° and 40° 2θ and several sharp

peaks, indicating that the sample is predominantly amorphous but also contains certain crystalline phases. Based on comparison with database cards, two crystalline components were identified: akermanite ($\text{Ca}_2(\text{Mg}_{0.75}\text{Al}_{0.25})(\text{Si}_{1.75}\text{Al}_{0.25}\text{O}_7)$), which is a common constituent of slags containing calcium, magnesium, aluminum, and silicon, and calcite (CaCO_3), which may form secondarily through carbonation (reaction with CO_2 from the air). The presence of a broad amorphous hump confirms a high content of the glassy phase, which is typical for granulated slag and is also a desirable property when used as a cement additive. The identified crystalline phases provide additional information about the composition and possible origin of the material.

The morphology of the prepared MOC with the slag was studied using SEM micrograph, as shown in Figure 2 at the highest magnification. Needle-like crystals typical of MOC Phase 5 can be seen. In the picture with higher magnification, defects can also be seen. This may be caused by imperfect adhesion between individual layers during the 3D printing process.

MOC phase 5 was also detected in the analyzed

FIGURE 3. The XRD diffraction pattern of MOC-GVS (CuK α).FIGURE 4. XRD pattern of GVS (CoK α).

sample by XRD (see Figure 3). The sample also contains CaCO_3 , which originates from GVS. According to XRF, the raw GVS contained a high amount of calcium, which was present both in crystalline form (as shown by XRD, Figure 4) and, most likely, also in an amorphous form, such as CaO , Ca(OH)_2 or calcium-rich silicates. When GVS was mixed into the MOC matrix, any calcium present as CaO would have first reacted with water to form Ca(OH)_2 . Subsequently, all Ca(OH)_2 could have undergone carbonation by exposure to atmospheric CO_2 , resulting in the formation of CaCO_3 .

Composition of the MOC-GVS analyzed by XRF can be seen in Table 3. Light elements in the table stand for elements from hydrogen to fluorine. On the elemental maps from EDS (see Figure 5), it can be

seen that magnesium, oxygen, and chloride are evenly distributed throughout the entire sample, which corresponds with the composition of MOC. Magnesium and chloride also originate from GVS, as well as silicon, aluminum, and calcium. Oxygen was detected by EDS in the amount of 48.9 wt.%, carbon 13.8 wt.%, magnesium 16.2 wt.%, and calcium 11.0 wt.%. Carbon detected by EDS can come from GVS or MOC, given its ability to carbonate.

XCT was deployed to study the internal structure of the printed sample. It was revealed that a considerable amount of unfilled volume resulted in high porosity, as can be seen in Figure 6. XCT data revealed equally distributed small pores in each printed layer without any shrinkage cracks together with relatively large defects originating at the bottom of the sample and

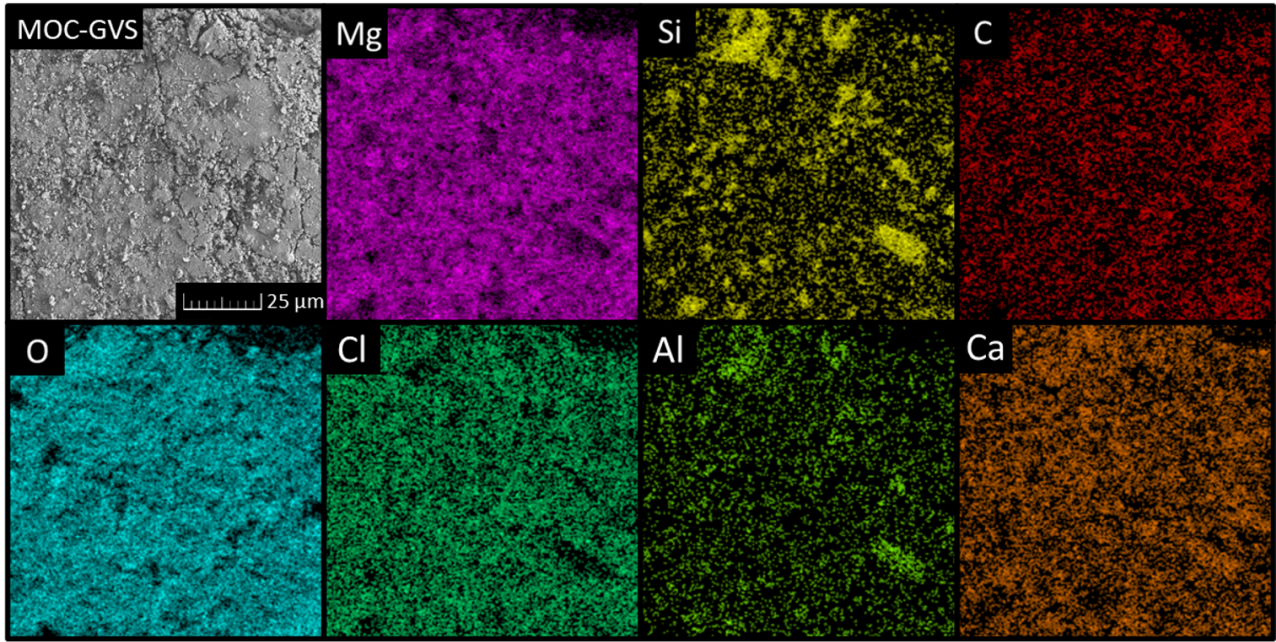


FIGURE 5. EDS elemental maps of MOC-GVS.

Element	wt.%	Element	wt.%
C + O + light elements	36.45	S	0.15
Ca	29.19	K	0.13
Mg	16.92	Na	0.12
Cl	10.43	Ti	0.12
Si	4.91	Ba	0.09
Al	0.93	W	0.04
Mn	0.30	Sr	0.04
Fe	0.16	P	0.02

TABLE 3. Content of elements in MOC-GVS obtained by XRF in wt.%.

growing towards the top following the printing direction. Moreover, such defects are connected horizontally showing intralayer disconnection. This is more visible when morphological analysis of identified pores is performed (see Figure 7). Morphological analysis as presented in Figure 7 revealed highly irregular pores as the majority of pores shows sphericity less than 0.7, while the obtained uni-directional porosity profile in Z-direction confirms the observation made from Figure 6 as the porosity reaches nearly 10 %.

After the XCT scan, the 3D printed cube was broken in half and then studied with OM. The image can be seen in Figure 8. From the picture, we can conclude the porous nature of the cube, aligning with the XCT scan data.

4. CONCLUSIONS

A 3D-printed MOC-based composite incorporating slag (GVS) was successfully fabricated. The printed specimen demonstrated the formation of the desired phase 5, confirming its compatibility with additive manufacturing techniques. This highlights MOC

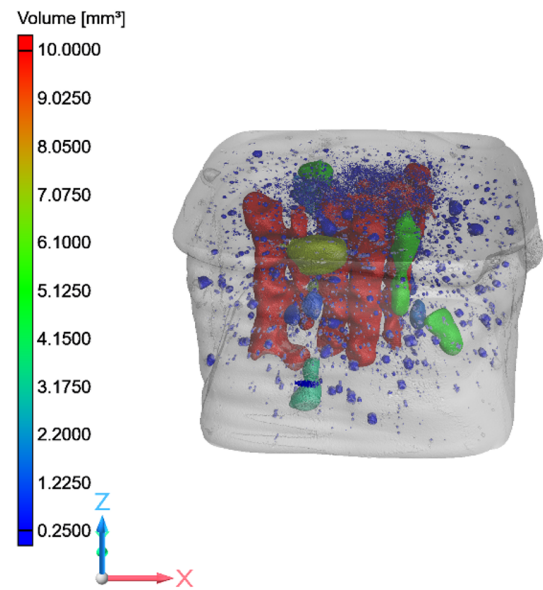


FIGURE 6. XCT image of the internal structure of a 3D printed cube of MOC-GVS.

phase 5 as a promising binder for 3D printing applications. Furthermore, the integration of GVS as a secondary raw material contributes to the environmental sustainability of the MOC. The MOC-GVS composite was thoroughly characterized in terms of its macro- and microstructure, phase, and chemical composition. The following experiments will focus on optimizing the 3D printing parameters to reduce porosity, improve volume filling, and enhance overall structural compactness.

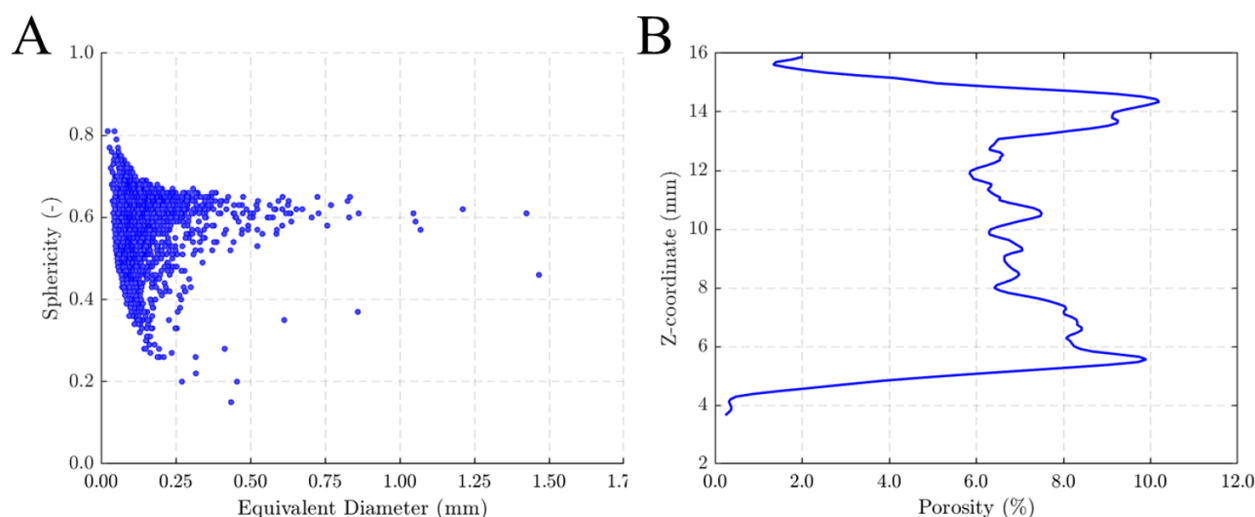


FIGURE 7. Morphological analysis of identified pores (A), and uni-directional porosity in Z-direction (B).

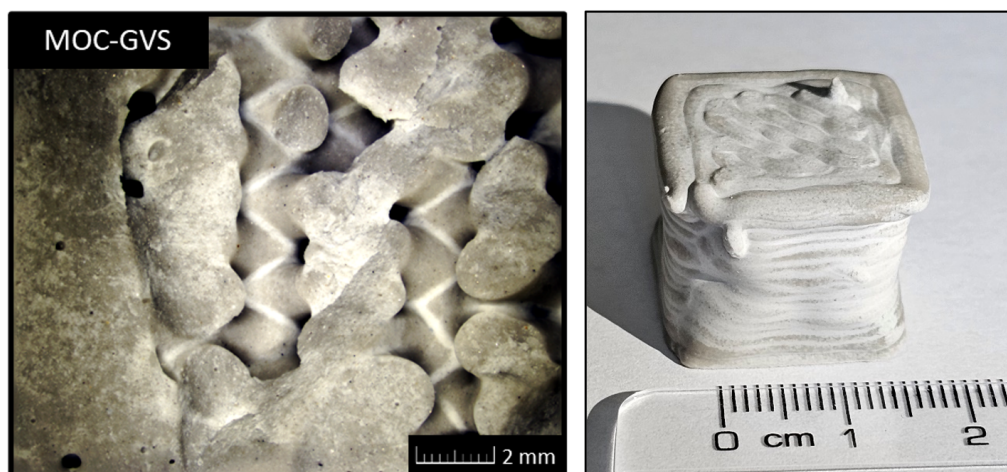


FIGURE 8. OM image (left) and a photography (right) of MOC-GVS 3D printed cube.

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